



A composite membrane based on a biocompatible cellulose as a host of gel polymer electrolyte for lithium ion batteries



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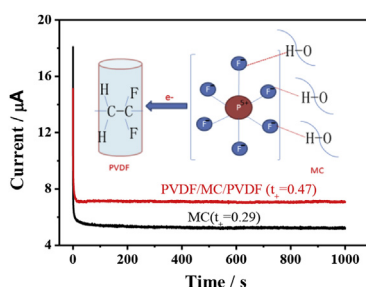
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HIGHLIGHTS

- Methyl cellulose (MC) is environmentally friendly and cheap.
- A composite polymer membrane is prepared by coating PVDF on the surface of a membrane from MC.
- The composite membrane is used as the separator and the host of a gel polymer electrolyte.
- The prepared gel polymer electrolyte shows excellent electrochemical performance.

GRAPHICAL ABSTRACT



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ABSTRACT

A composite polymer membrane is prepared by coating poly(vinylidene fluoride) (PVDF) on the surface of a membrane based on methyl cellulose (MC) which is environmentally friendly and cheap. Its characteristics are investigated by scanning electron microscopy, FT-IR, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The outer PVDF layers are porous which results in high electrolyte uptake and the lithium ion transference number is much larger than that of the pure MC. Moreover, the cell based on Li/LiFePO₄ delivers high discharge capacity and good rate behavior in the range of 4.2–2.5 V when the composite membrane is used as the separator and the host of a gel polymer electrolyte, lithium as the counter and reference electrode, and LiFePO₄ as cathode. The obtained results suggest that this unique composite membrane shows great attraction in the lithium ion batteries with high safety and low cost.

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1. Introduction

Rechargeable lithium ion batteries have become a commercial reality in recent years. They are widely used in mobile electronic equipment, such as computers, cell phones and so on [1–3].

Conventional lithium ion batteries used liquid electrolyte, which made the batteries unsafe because of electrolyte leakage. Now this problem has been suggested to solve by polymer electrolytes. Until now, polymer electrolytes based on polyacrylonitrile (PAN) [4–6], poly(ethylene oxide) (PEO) [7–9], poly esters [10–12] and poly(vinylidene fluoride) (PVDF) [13–15] have been widely studied. Recently, the poly(vinylidene fluoride) (PVDF) has been identified as a potential host for lithium polymer batteries because of its appealing properties. This polymer host is expected to be more anodically stable because of the strong electron-withdrawing functional group (–C–F) [16–20]. However, its practical

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application is still not realized due to its high cost, which greatly limits the commercialization of electric vehicles.

Formerly we reported its composites with nonwoven fabrics and glass fiber mats, which can sharply decrease the cost together with excellent electrochemical performance [21,22]. However, both nonwoven fabrics and glass fiber mats are too thick and too heavy, and will lead to a decrease of volumetric and gravimetric energy densities of the prepared lithium ion batteries. Recently, we found that methyl cellulose (MC) can be a host of gel polymer electrolyte for lithium ion batteries leading to higher ionic conductivity and higher lithium ion transference number than the commercial separator [23]. However, due to the existence of the remaining hydroxyl groups in MC, the difference between charge and discharge voltages is larger than that for the commercial separators, and the rate capability of lithium ion batteries could not be improved.

Cellulose is the most abundant polysaccharide, and occurs mainly within the cell wall of higher plants as a structural material. Cellulose is a linear macromolecule consisting of (1–4) linked β -D-glucopyranosyl monomers, and this β -(1–4) configuration contributes to its rigid structure and to the formation of aggregates through intra- or inter-molecular hydrogen bonds via hydroxyl groups [24]. When some or even all of the hydrogen atom in the hydroxyl group were replaced by methyl group, the cellulose becomes MC, which is widely used in construction, food, cosmetics industry as an environmentally friendly and economic polymers. These results suggest great promise for its application as a host of gel polymer electrolytes for lithium ion batteries.

In order to overcome the problems of MC, here we reported a composite membrane which consists of sandwiched structure of PVDF/MC/PVDF. The composite membrane has good mechanical property and relatively high ionic conductivity. Moreover, it produces no pollutant during the preparation because MC is nontoxic and the solvent water is harmless, which made our work very significant. It can meet the great demand for highly efficient and

mobile energy storage, which furthermore is sustainable from an economic and environmental point of view.

2. Experimental

MC (100 mg, Aldrich) was dissolved in distilled water (40 mL) at room temperature with constant stirring, then the solution was casted on a glass plate. After the solvent was vaporized at 80 °C, a thin MC membrane with the thickness of 20 μm was obtained. For comparison, a sandwiched membrane PVDF/MC/PVDF was prepared as follows: a home-made PVDF membrane from electrospinning (30 kV at a GVR-200 Instrument of Fuerma Company, Beijing, with diameter of the spinhole of 0.06 mm) was coated on a piece of glass, then a little water was added on the upper surface of the PVDF membrane. After that, the prepared MC membrane was rolled onto the PVDF membrane. Later another layer of PVDF was coated on the MC layer in the same way. After vaporizing the water, a sandwiched membrane PVDF/MC/PVDF with thickness of 60 μm was obtained. The membrane was further dried under vacuum at 80 °C for 24 h to remove the residual solvent prior to measurement and use.

The surface morphology of the prepared membranes was examined by means of scanning electron microscope (SEM, Philip XL30). The specimens for the SEM micrographs of the cross-section of the membranes were prepared by fracturing them in liquid nitrogen. FT-IR measurement was carried out on a BRUKER VECTOR-22 spectrometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the membranes were carried out by utilizing a Perkin–Elmer TGA7/DSC7. The thickness of the membranes was measured with a micrometer (SM & CTW, Shanghai). Stress–strain tests were conducted by using a Sansi YG832 tensile testing machine with a crosshead speed of 1 mm min^{−1}.

The calculation of the amount of liquid electrolyte uptake is referred to the equation: $\eta = (w_t - w_o)/w_o \times 100\%$, where w_o and w_t

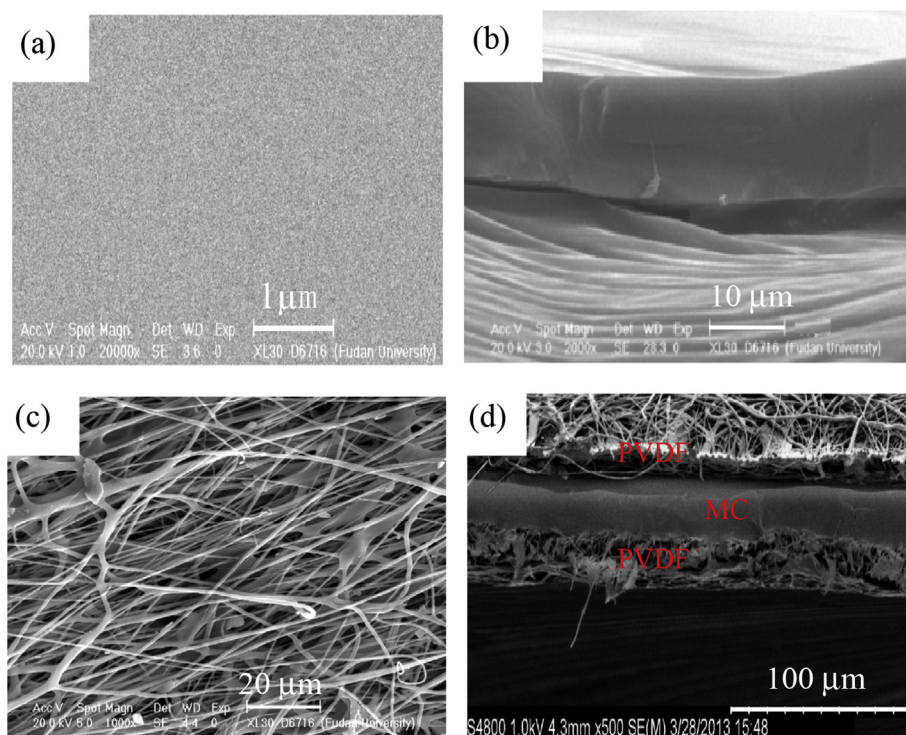


Fig. 1. SEM micrographs of (a) the surface and (b) cross section of MC, (c) the surface of PVDF and (d) the cross section of the sandwiched membrane PVDF/MC/PVDF.

are the weight of the membranes before and after absorbing the organic electrolyte (1 M LiPF₆ solution in EC/DEM/EMC, 1/1/1, w/w/w, Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd.). The ionic conductivities were measured in the temperature range 298–348 K by using an electrochemical working station CHI660C (Chenhua) in the frequency range 10 Hz–100 kHz. The membranes were sandwiched between two stainless steel electrodes of 2.54 cm² in area for conductivity measurement. The electrochemical window of the gel polymer electrolytes was determined from the linear sweep voltammogram which was carried out by the electrochemical working station using a two-electrode cell. Stainless steel was used as the working electrode and lithium foil as the counter and reference electrode, respectively. The measurement was done between 0 V and 6 V (vs. Li⁺/Li) at the scan rate of 1 mV s⁻¹.

Electrochemical performance of the membrane in lithium batteries was evaluated by coin-type cell, where lithium foil was used as the counter and reference electrode, and the mixture of LiFePO₄ (STL Energy Technology Co., Ltd.), acetylene black and PVDF in the weight ratio of 8:1:1 as the working electrode. The membranes were immersed in the organic electrolyte for 12 h to become a gel polymer electrolyte [25], then used as the separator and the electrolyte. The cycling performance of the cells was carried out by a Land battery tester with the current density of 0.1C between 2.5 and 4.2 V.

3. Results and discussion

Fig. 1(a) and (c) presents the scanning electron micrographs (SEM) of the surface of the membrane MC and PVDF. It is clear that the coating layer PVDF presents porous and fiber structure. The diameter of the fibers is in the range of 100–500 nm and the membrane consists of quite some layers of the electrospun PVDF. As a result, the thickness of the PVDF film, 20 μm, is very uniform. The inside MC membrane shows relatively smooth surface. From the cross-sectional micrograph shown in Fig. 1(b) and (d), it is found that the inside of MC is solid. In contrast, the membrane PVDF/MC/PVDF consists of three layers. The middle layer is MC which is sandwiched by two PVDF layers.

Fig. 2(a) shows the IR spectra of MC, PVDF and the composite membrane PVDF/MC/PVDF. The characteristic absorption peak of MC are observed at 3446 cm⁻¹ (O–H stretching), 3000–2800 cm⁻¹ (C–H stretching in CH₂ and CH₃), 1646 cm⁻¹ (C–C ring stretching), 1456 cm⁻¹ (C–H bending in CH₂), 1300–1000 cm⁻¹ (C–O stretching) [24]. The typical peaks of PVDF are 1400 cm⁻¹ (deformation vibration band of –CH₂–), 1072 cm⁻¹ (stretching band of C–C), 882 cm⁻¹ (band for amorphous phase) and 841 cm⁻¹ (rocking band of –CH₂–) [26]. In the case of PVDF/MC/PVDF, all the typical peaks of PVDF and MC are present clearly. This indicates that the composite PVDF/MC/PVDF is successfully obtained.

Fig. 2(b) shows the stress–strain curves of the polymer membranes for MC, PVDF and PVDF/MC/PVDF. The maximum strain of the membrane PVDF/MC/PVDF is 22.5%, which is nearly as large as the pure MC. However, in terms of the maximum stress, the sandwiched membrane PVDF/MC/PVDF is 28.4 MPa, which is much higher than that of the pure MC. This is resulted from the coating layer PVDF whose maximum stress is as high as 31.5 MPa.

The thermal stability is an important property for polymer electrolyte during application in lithium ion batteries [21,27]. It can be seen from Fig. 3(a) that MC does not appear obvious weight loss until 300 °C and the endotherm begins at about 300 °C in the DSC curve of MC in Fig. 3(b). Moreover, there is no sharp endothermic peak in the DSC curve of MC until 350 °C which is the decomposition temperature of MC. We also can find this sharp endothermic peak in the DSC curve of the

sandwiched composite membrane PVDF/MC/PVDF. Besides, there is another sharp endothermic peak in the DSC curve of the composite membrane at 170 °C, which is the melt point of the pure PVDF. The retention ability of electrolytes is crucial to the safety of lithium ion batteries [28]. The thermogravimetry and differential scanning calorimetry (TG–DSC) curves of the membrane MC and PVDF/MC/PVDF soaked with the same amount of the electrolyte (0.1 mL mg⁻¹) are shown in Fig. 3(c) and (d). The organic electrolyte in the MC begins to evaporate at about 80 °C and is rapidly evaporated at about 110 °C which is indicated by the sharp endothermic peak in the DSC curve of MC. In terms of PVDF/MC/PVDF, the absorbed electrolyte starts to evaporate at 65 °C, but the evaporation rate is much slower than that of the pure MC. This is mainly due to the coating layer PVDF which can effectively slow down the evaporation of the solvents due to the formation of gelled polymer electrolytes [21,22,29–32].

The ionic conductivity of the membrane plays a crucial role on whether the membrane can be used in lithium ion batteries and has a great influence on the electrochemical performance. Fig. 4 shows the dependence of ionic conductivity on temperature ranged from 25 to 75 °C of the membranes saturated in the organic electrolyte. The conductivity was calculated from the impedance plots which are shown in Fig. 4(a) and (b). The ionic conductivity increases with temperature, a typical Arrhenius behavior of lithium polymer electrolytes [13]. The activation energies for the movement of ions are 13.48 and 5.95 kJ mol⁻¹, respectively, for the MC and PVDF/MC/PVDF separator. The main reason is due to different host. The polymer host PVDF is anodically very stable because of the strong electron-withdrawing functional group (–C–F). The movement of ions in the PVDF host is easier than that in the MC host. As a result, the activation

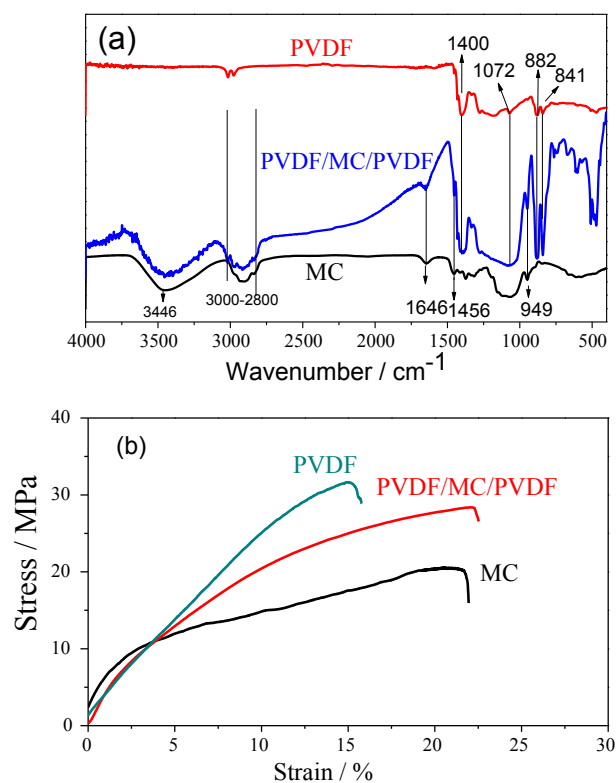


Fig. 2. (a) FT-IR spectra of the membrane MC, PVDF and the sandwiched membrane PVDF/MC/PVDF, and (b) stress–strain curves of the polymer membranes PVDF, PVDF/MC/PVDF and MC.

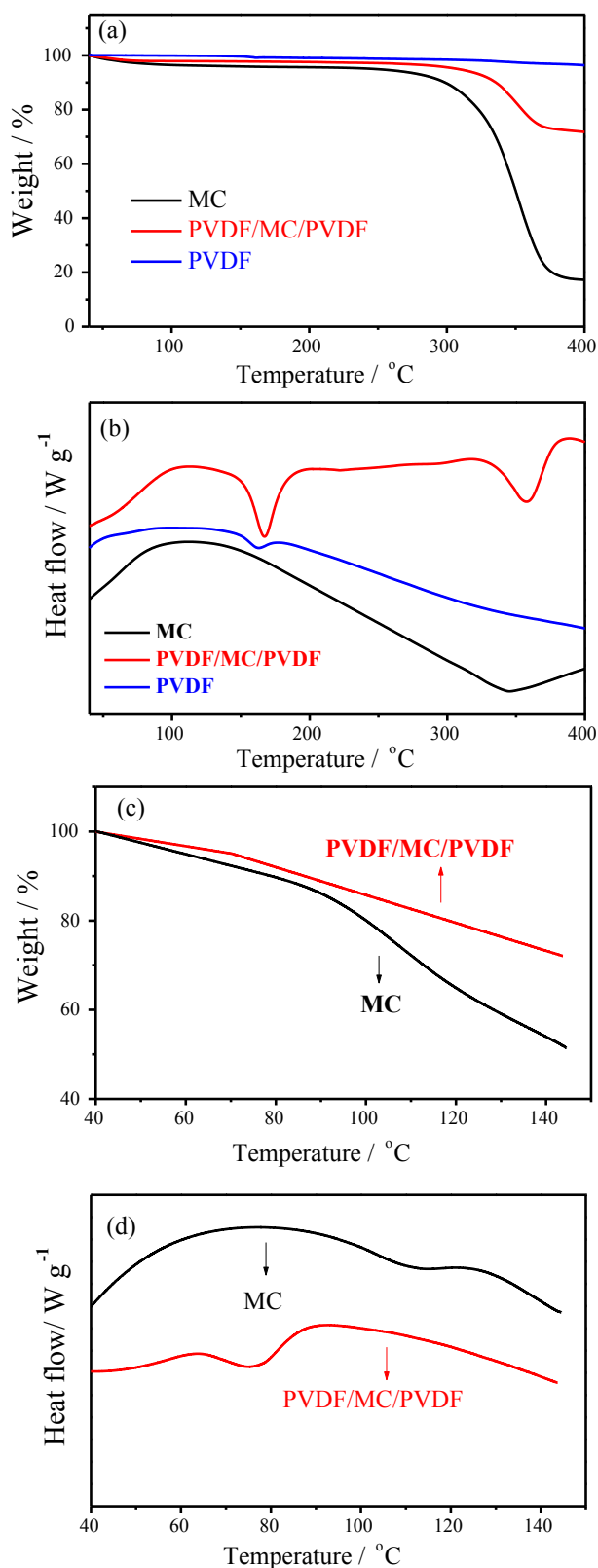


Fig. 3. (a) Thermogravimetry (TG) and (b) differential scanning calorimetry (DSC) curves of the polymer membranes MC, PVDF and PVDF/MC/PVDF, (c) TG and (d) DSC curves of the polymer membranes MC and PVDF/MC/PVDF after absorbing the same weight amount of 1 M LiPF₆ electrolyte.

energy of the composite polymer electrolyte PVDF/MC/PVDF is lower than that of the MC separator. The ionic conductivity of PVDF/MC/PVDF at 25 °C is 1.5 mS cm⁻¹, much higher than that of the pure MC (0.2 mS cm⁻¹). This is due to the high electrolyte absorption of the composite membrane PVDF/MC/PVDF (138.6 wt.%), while the electrolyte uptake ratio of the membrane MC is only 73.4 wt.%.

For determining the electrochemical stability window of the polymer electrolytes, a linear sweep voltammetry experiment was performed in the potential range of 0–6.0 V (vs. Li⁺/Li) at a scan rate of 2 mV s⁻¹. Fig. 5(a) shows that the current flow is very small when the voltage is below 4.8 V (vs. Li⁺/Li), which makes them very suitable for the application in lithium ion batteries. The lithium ion transference number, t_+ , is an important parameter for rechargeable lithium ion batteries [33–35]. From Fig. 5(b), it can be found

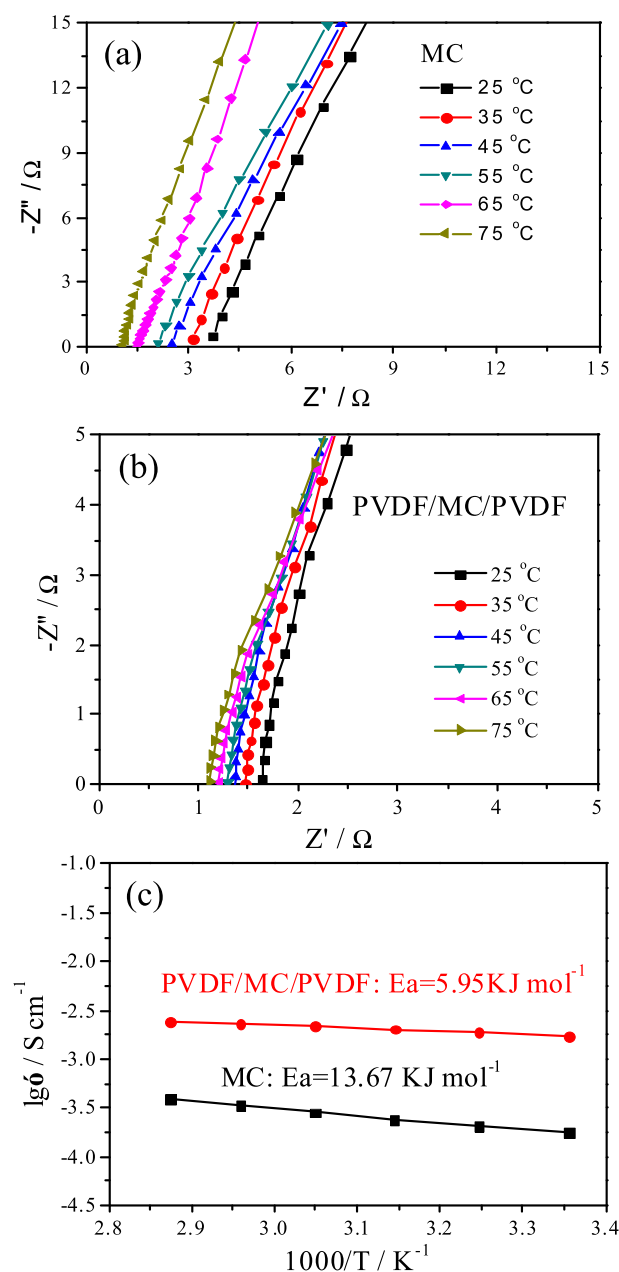


Fig. 4. Impedance plots of the gel polymer electrolytes based on (a) MC and (b) PVDF/MC/PVDF (with the saturated amount of electrolyte) at different temperatures, and (c) Arrhenius plots of the gel polymer electrolytes based on MC and PVDF/MC/PVDF.

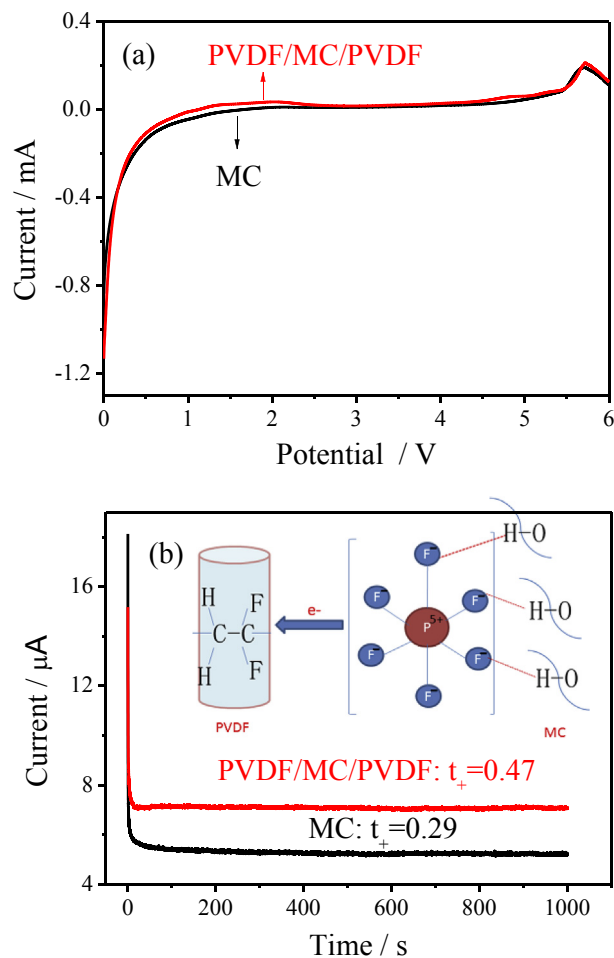


Fig. 5. (a) Linear sweep voltammograms of MC and PVDF/MC/PVDF membranes after saturated in 1 M LiPF_6 electrolyte, and (b) chronoamperometry profiles for MC and PVDF/MC/PVDF at 25 °C in block cells using Li metal as both electrodes with step potential of 10 mV.

that the lithium ion transference number [36] of the electrolyte composition PVDF/MC/PVDF is 0.47, much larger than that of the polymer electrolyte MC (0.29). One reason is perhaps due to the polarity of the PVDF matrix, which hinders the movement of large PF_6^- anions and assists the movement of Li^+ ions [22,37]. Another reason can be ascribed to the surface of the MC pores, which has some hydroxyl groups that are easy to form hydrogen bond with fluorine atom in PF_6^- . The interaction hinders the movement of the anions in the electrolyte and improves the lithium ion transference number, which is schematically illustrated in the inset of Fig. 5(b). This relatively high t^+ can ensure the battery operation under a high current density since the overpotential or polarization will be much smaller.

The electrochemical performances of the gel MC membrane and composite polymer electrolyte PVDF/MC/PVDF were evaluated by assembling batteries which used LiFePO_4 as the cathode and Li metal as the counter and reference electrode. The charge–discharge curves for the LiFePO_4 cathodes tested at the rate of 0.2C are shown in discharge curves for the PVDF/MC/PVDF gel polymer electrolyte is about 0.2 V, much smaller than that for the pure MC (0.4 V). The reversible capacity of the LiFePO_4 for the gel membrane PVDF/MC/PVDF is about 150 mAh g^{-1} at 0.2C, which is also higher than that for the MC separator, about 130 mAh g^{-1} . This is due to the higher lithium ion transference number and higher

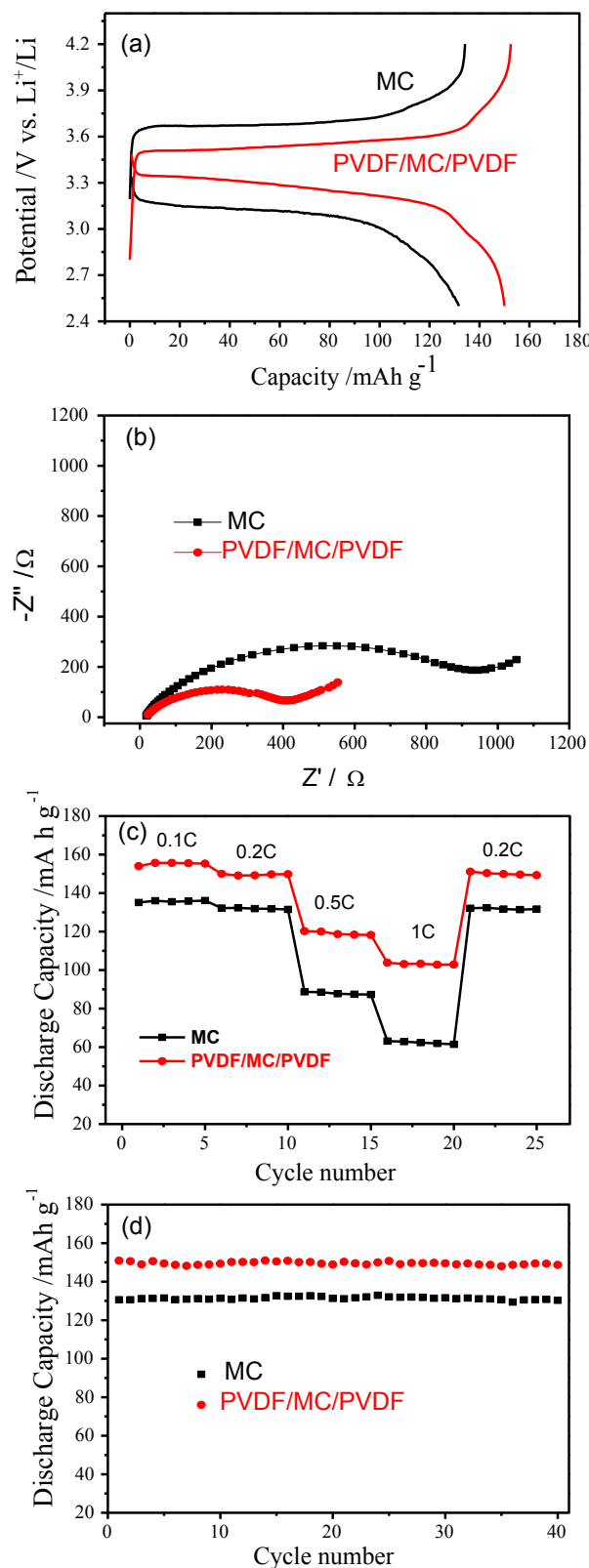


Fig. 6. Electrochemical performance of LiFePO_4 tested by using MC and the PVDF/MC/PVDF sandwiched membrane as separators, respectively, saturated with 1 mol L^{-1} LiPF_6 electrolyte and Li metal as the counter electrode: (a) charge–discharge curve and (b) the ac impedance spectra of the cells before cycling; (c) rate behavior, and (d) cycling behavior.

ionic conductivity in the PVDF/MC/PVDF composite polymer electrolyte than those in the MC polymer electrolyte.

From the AC impedance spectra shown in Fig. 6(b), it can be seen that the charge transference resistance for the composite gel polymer electrolyte PVDF/MC/PVDF is smaller than that for the MC gel polymer electrolyte. The smaller charge transference resistance is due to good surface layer of the composite membrane since PVDF is much more stable with Li metal than MC, which has some remaining hydroxyl groups. In Fig. 6(c), when tested at different current densities such as 0.1C, 0.2C, 0.5C and 1C, it still keeps higher discharge capacity than those for the MC membrane saturated with the liquid electrolyte. This is not only due to the higher transference number of Li^+ and higher ionic conductivity but also to the smaller charge transference resistance for the gel polymer electrolyte based on the composite membrane PVDF/MC/PVDF. When tested at the charge and discharge rate of 1C, the LiFePO_4 still presents a discharge capacity of 110 mAh g^{-1} . The cycling performance of LiFePO_4 between 2.5 and 4.2 V (vs. Li^+/Li) using the gel polymer electrolytes at 0.2C (34 mA g^{-1}) is very good (Fig. 6(d)), similar to that of the commercial separator [22]. After 40 cycles there is still no evidence of capacity fading.

Our above results show that the ionic conductivity of lithium ions and lithium ion transference number in the gel composite polymer electrolyte PVDF/MC/PVDF are both larger than that in the MC separator saturated with the liquid electrolyte. As a result, a higher reversible capacity for the LiFePO_4 and a better rate capability are achieved. In the case of the overpotential during charge and discharge process, it is mainly dependent on the interface resistance in our case though it is well known that the transportation of lithium ion is important.

4. Conclusions

Methyl cellulose (MC), which is environmentally friendly and cheap, is successfully modified as a host of a gel polymer electrolyte with excellent electrochemical performance. After the polymer membrane MC was sandwiched by two electrospinning poly(vinylidene fluoride) (PVDF) membranes, the obtained composite membrane PVDF/MC/PVDF exhibits good mechanical property and excellent thermal stability. Comparing with the pure gel polymer electrolyte based on MC, the ionic conductivity of that based on the composite PVDF/MC/PVDF is much higher, which is up to 1.5 mS cm^{-1} at room temperature. In addition, the lithium ion transference number of the gel polymer electrolyte based on the composite PVDF/MC/PVDF is much increased at room temperature. When the gel polymer electrolyte based on the composite is used as the separator and the polymer electrolyte, the above results lead the batteries to present a high discharge capacity and a good rate performance. All the above results indicate great promise for practical application of this polymer electrolyte based on the composite PVDF/MC/PVDF.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2014.07.058>.

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